



TITLE:

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(Commemoration Issue Dedicated to Professor Hiroshi Ibagaki, Professor Michio Kurata, Professor Ryoza Kitamura, On the Occasion of Their Retirements)

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CITATION:

Ohnuma, Hiroshi ...[et al]. Chemical Modification of Poly(styrene-b-butadiene-b-4-vinyl pyridine) Three-Block Polymers of ABC Type (Commemoration Issue Dedicated to Professor Hiroshi Ibagaki, Professor Michio Kurata, Professor Ryoza Kitamura, On the Occasion of Their Retirements). Bulletin of the Institute for Chemical Research, Kyoto Universit ...

ISSUE DATE:

1989-02-15

URL:

<http://hdl.handle.net/2433/77233>

RIGHT:

Chemical Modification of Poly(styrene-*b*-butadiene-*b*-4-vinyl pyridine) Three-Block Polymers of ABC Type.

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Received September 29, 1988

For poly(styrene(S)-*b*-butadiene(B)-*b*-4-vinyl pyridine(P)) three-block polymers, in which two typical morphologies, i.e., a "ball-in-a-box" and a "three-layer-lamella" structure, are revealed depending on casting conditions, quaternization of the P blocks, crosslinking of the B blocks and sulfonation of the S blocks were examined in that order. The reagents and the reaction conditions were studied in detail. The degree of reaction with reaction time was followed by elemental analysis, IR spectroscopy, ESCA and ion-exchange capacity measurements. The morphological changes after the chemical modification were observed by transmission electron microscopy. The "ball-in-a-box" morphology of the original film was maintained through the quaternization and crosslinking reactions, but destroyed after the sulfonation reaction.

KEY WORDS: Poly(styrene-*b*-butadiene-*b*-4-vinyl pyridine)/ Quaternization/
Crosslinking/ Sulfonation/ Morphology/

INTRODUCTION

In our previous publications,²⁻⁶ we described synthesis, morphology and mechanical properties of poly(styrene-*b*-butadiene-*b*-4-vinyl pyridine) three-block polymers of ABC type, referred to as SBP polymers. The SBP polymers with nearly equivolume composition cast from suitable solvents exhibited two different types of unique morphology.²⁻⁵ One was a "ball-in-box" morphology, in which poly(4-vinyl pyridine) (P) spherical domains surrounded by polybutadiene (B) segments were dispersed in a continuous polystyrene (S) matrix. The other was a "three-layer-lamella" morphology, in which three components formed continuous phases in a regular periodic fashion. The solvents such as chloroform (CHCl₃) produced the former type of morphology, while the binary mixtures of *n*-butyraldehyde (BA)/CHCl₃ (9/1 v/v) or tetrahydrofuran (THF)/methanol (MeOH) (4/1 and 9/1 v/v) produced the latter type.

To explore the possibility of utilizing these SBP polymers as special function materials such as charge mosaic membranes for piezodialysis^{7,8} and biocompatible materials,⁹⁻¹¹ we planed to modify these polymers without destroying the original morphology of the as-cast membranes as long as possible. Fujimoto et al.¹²⁻¹⁶ have reported a series of studies along the same line. They synthesized poly[styrene-*b*-isoprene-*b*-(4-vinylbenzyl)dimethylamine] three-block polymers of SIA type,¹² and three component penta-block polymers of ISIAI type,¹³⁻¹⁴ and modified these polymers to obtain charge mosaic membranes with three lamellar structure.^{15,16} However, they did

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not carry out the detailed analysis on the change of the degree of reaction with reaction time and the chemical characterization of modified membranes at each reaction step. We cast the SBP polymers from adequate solvents, and attempted first to quaternize the P blocks,^{6,16} then to introduce crosslinks in B blocks,¹⁷ and finally to sulfonate the S blocks.^{17,18} We also cast the SBP polymers on the surface of polyethylene tubings and subjected to chemical modification by the similar procedures for a blood compatibility test.⁹ To achieve a satisfactory modification of these as-cast SBP polymer membranes, we examined the necessary reaction conditions in detail and carried out surface characterization and morphology observation, particularly on those initially having a "ball-in-a-box" morphology, at each stage of the reactions. In this paper, we report the results on the chemical modifications of SBP polymer films and their surface analysis.

EXPERIMENTAL

Polymer Samples and Films. The SBP polymers were synthesized by a living anionic polymerization method under high vacuum (10^{-6} torr).^{2,3,5} The reaction consisted of a three-stage sequential addition of styrene, butadiene, and 4-vinyl pyridine in benzene with *sec*-butyllithium as the primary initiator of styrene. At the end of the first and second steps, aliquots were taken to recover the S precursor and the SB intermediate, respectively, for later characterization. The polymers were characterized by gel permeation chromatography (GPC), UV absorption, ultracentrifugation, and osmometry in CHCl_3 . The sedimentation velocity patterns revealed that the molecular weight distributions are fairly narrow and no unreacted S and SB precursors exist in the SBP polymers. The number average molecular weights, M_n , agreed with the stoichiometric values, as anticipated. The details were reported previously.^{2,3,5} Table I shows the characteristics of the samples used in this study.

Table I. Characteristics of the SBP Samples

Code	$10^{-3} M_n^S$	S Block		B Block		P Block		SBP Polymer
		(mol %)	$(M_w/M_n)^S$	$10^{-3} M_n^B$	(mol %)	$10^{-3} M_n^P$	(mol %)	
SBP-11	23.3	(0.332)	1.08	14.2	(0.390)	19.7	(0.278)	57.2
SBP-12	13.3	(0.198)	1.06	15.6	(0.447)	24.1	(0.355)	53.0

In most experiments, we used SBP polymer films cast from CHCl_3 with the "ball-in-a-box" morphology and occasionally those cast from BA/CHCl_3 (9/1 v/v) and THF/MeOH (9/1 v/v) mixtures with the "three-layer-lamella" morphology. Films of a commercially available SBS sample (Kraton 1101, Shell Chemical Co., $M_n=8.03 \times 10^4$, styrene content 33 wt%) cast from cyclohexane solution were used as a control in each of modification reactions. The films used were of 5–200 μm thick.

Reagents. All the reagents used in the modification reactions were purified by usual methods just before use.

IR Spectroscopy. Conventional IR and FT-IR measurements were carried out on JASCO DS-21 or A-102 grating infrared spectrometers and a JASCO FT/IR-3 Spectro-

meter (Japan Spectroscopic Co., LTD.), respectively. FT-IR ATR spectra were measured with a KRS-5 reflecting plate as an internal reflecting element.

ESCA. ESCA spectra were obtained with AEI ES 200 Spectrometer and a Shimadzu Electron Spectrometer ESCA 750. The X-ray sources were Al $K\alpha_{1,2}$ and Mg $\alpha_{1,2}$ with corresponding photon energy of 1486.6 and 1253.7 eV, respectively. The binding energy (BE) value was calibrated using 285.0 eV for the C_{1s} core level of the hydrocarbon as an internal reference.

Morphology Observation. Usually the films were exposed to a 1% aqueous solution of osmium tetroxide (OsO_4). The sulfonated films were immersed in a 1 M aqueous solution of lead acetate, which stained the sulfonated S block selectively, and then treated with OsO_4 . The stained films were microtomed to obtain ultrathin sections of usually 60 nm thickness in the direction normal to the film surface, and observed with Hitachi Model HU-12 and H 600 Transmission Electron Microscopes.

Measurements of Ion-Exchange Capacities. The ion-exchange capacities of the chemically modified films were determined by titrimetric methods. To determine the amount of sulfonic acid groups, we immersed a film in a 1 N HCl solution for 24 h at room temperature, thoroughly rinsed with distilled water and dried at 100°C under vacuum for 2 days. After the weighed film was equilibrated with a 1 N NaCl solution for 2 days at room temperature, the solution was titrated with a 0.1 N NaOH solution with use of a SelectIon Analyzer (Beckman Instrument Co., Type 5000) equipped with a Futara 10-mm combination electrode (39504). The cation-exchange capacity per dry weight of the polymer film (C^+ m eq/g) was calculated by subtracting the blank value for the same volume of the 1 N NaCl solution.

For the analysis of quaternary ammonium groups, a film was immersed in a 1N KCl solution for 24 h at room temperature. It was then thoroughly rinsed with distilled water, transferred into a 1 N $NaNO_3$ solution and kept for 2 more days at room temperature. The chloride ion content in the solution was determined by Volhard titration method with a 0.1 N NH_4SCN solution. The anion-exchange capacity (C^- m eq/g) was calculated from the chloride ion content in the solution and dry weight of the film.

RESULTS AND DISCUSSION

Quaternization of P Block

The quaternization of P block was examined with methyl bromide (CH_3Br) by the vapor method as reported by Platt and Schindler.^{19,6} SBP films with different morphology, freeze-dried SBS samples, and an SBS film as control were used in this experiment. The sample was placed in a separable flask and dried under vacuum at room temperature for 24 h. After drying, CH_3Br was introduced into the flask and kept at 70°C for 48 h. The reacted sample was dried under vacuum for several days to remove unreacted CH_3Br . Table II summarizes the forms and morphologies of the SBP samples used for the quaternization and the results of elemental analysis of the quaternized samples. The ratio of Br to N is very close to one for all the samples tested, showing that the degree of quaternization is 100% within the experimental error.

Table II. Results of Elemental Analysis of Quaternized SBP Samples

Sample Code	Form	Casting Solvent	Pressure of CH ₃ Br/atm	Elemental Analysis (wt %)				Mol Ratio ^c of Br/N
				C	H	N	Br	
SBP-11	Film	CHCl ₃ ^a	0.36	62.32	7.36	2.95	17.20	1.02
	Freeze-dried		0.68	68.03	7.35	2.92	16.56	0.99
SBP-12	Film	CHCl ₃ ^a	—	59.32	6.97	4.15	23.77	1.00
	Film	THF/MeOH (9/1) ^b	0.36	59.41	6.95	3.95	22.55	1.00
	Freeze-dried		0.68	59.38	6.95	4.06	23.16	1.00
SBS	Film	Cyclohexane	0.68				0.00	0.00

a. "ball-in-a-box" morphology b. "three-layer-lamella" morphology c. calculated from the results of elemental analysis.

The result means that the reaction proceeded to a perfection regardless of the sample form and morphology. As expected, Br was not detected in the SBS film used as the control. The comparison of IR spectra before and after the quaternization showed that the absorption band of the pyridine ring at 1595 cm⁻¹ disappeared by the reaction, and two new absorption bands of quaternary pyridinium salt emerged at 1490 cm⁻¹ and 1640 cm⁻¹. These finding show that CH₃Br preferentially reacted with the nitrogens of the pyridine rings.

Electron micrographs before and after the quaternization of several SBP films cast from two different types of solvent systems were reported previously.⁶ Those micrographs revealed that, in all cases, the original domain shapes remain unchanged, but the sizes and spacings of P domains slightly increased by quaternization. Therefore, it was concluded that the complete quaternization of the P blocks in SBP films could be carried out without morphological changes under the gas-phase quaternization mentioned above.⁶

Crosslinking of B Block

To carry out crosslinking reaction of B blocks with sulfur monochloride (S₂Cl₂), we searched for solvents which neither dissolve the polymer films nor react with S₂Cl₂. Acetonitrile (CH₃CN), nitromethane (CH₃NO₂) and dibutylphthalate (DBP) were found desirable. First, to determine the sufficient reaction time, we tested crosslinking of SBS films. For the convenience of later IR analysis, rather thin films of 5–7 μm thick were used. The film were dipped into 5% (v/v) S₂Cl₂ solution in CH₃CN at room temperature, and allowed to react with. During the time course of reaction, a film was taken out, thoroughly rinsed with 10% (v/v) CS₂ solution in *n*-hexane, and dried under vacuum of 10⁻³ torr at room temperature for 2 days. The progress of the reaction was followed by IR measurements.

Figure 1 shows the IR spectra of the original SBS film and those reacted for 5 and 150 min. The absorption bands at 911 cm⁻¹ and 963 cm⁻¹ corresponding, respectively, to 1, 2-vinyl and 1, 4-*trans* C=C double bonds of B blocks decrease with the reaction time. The degree of residual unsaturation estimated from these absorption bands is shown in Figure 2. In the analysis, the absorption band of styrene at 1495 cm⁻¹ was

Poly(styrene-*b*-Butadiene-*b*-4-vinyl pyridine

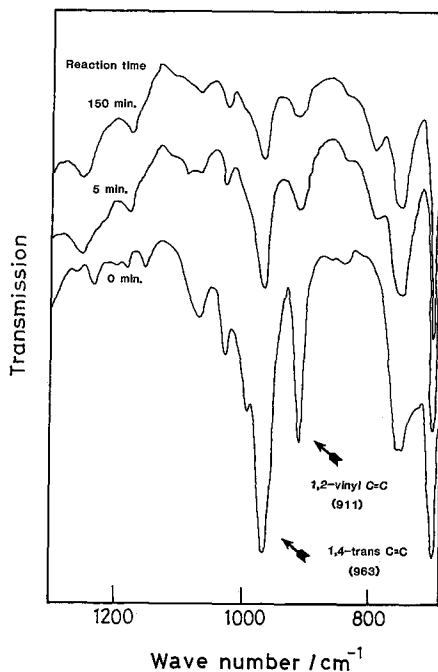


Figure 1. Change in the IR spectra of an SBS film by the reaction with S₂Cl₂ for 5 and 150 min.

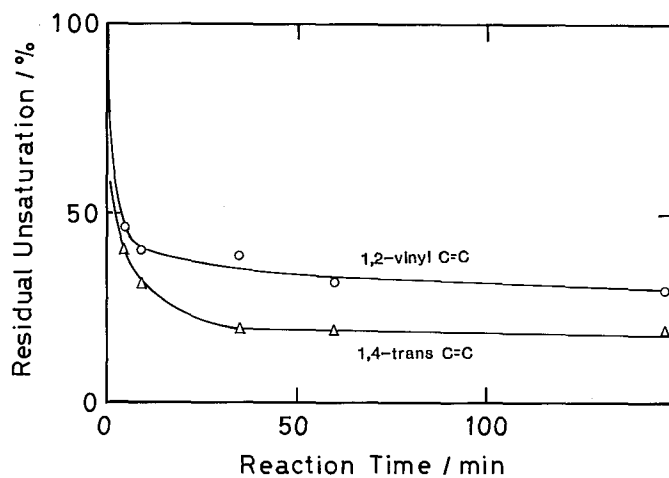


Figure 2. Change of the degree of residual unsaturation for 1, 2-vinyl (○) and 1, 4-*trans* (△) double bonds in the crosslinking reaction with the reaction time.

chosen as an internal standard. The reaction proceeds rapidly in early 15 min, and then slowly. Even after 150 min, 20% of 1, 4-*trans* double bonds and 30% of 1, 2-vinyl double bonds remain unreacted. The reaction in CH₃NO₂ was similar to that in CH₃CN.

A quaternized SBP film abbreviated as SBP(Q) was subjected to 10 % (v/v) S_2Cl_2 solution in CH_3CN for 150 min to obtain a SB(X)P(Q) film. Unfortunately, since the IR absorption bands for C=C double bonds of SB(X)P(Q) were not clearly identified due to the overlapping of many bands, the degree of residual unsaturation could not be determined by the IR method. However, we guess that the situation might be similar to the case of an SBS film, as there is not a large difference in the microstructures of the B sequence between SBS and SBP polymers (8% 1, 2-vinyl, 37% *cis*-1, 4, and 55% *trans*-1, 4 for SBS,²⁰ and 10% 1, 2-vinyl, 39% *cis*-1, 4, and 51% *trans*-1, 4 for SBP⁶). Figure 3 compares the electron micrographs of a SBP-12 film cast from $CHCl_3$, SBP-12/ $CHCl_3$, and subsequently quaternized and crosslinked SB(X)P(Q)-12/ $CHCl_3$. Evidently, the “ball-in-a-box” morphology was unaltered by gas-phase quaternization and crosslinking employed. The same was the case for the film with the “three-layer-lamella” morphology.

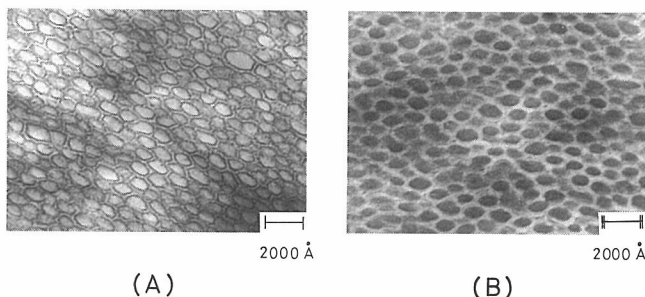


Figure 3. Electron micrographs of a SBP-12 film cast from $CHCl_3$, SBP-12/ $CHCl_3$ (A), and that quaternized and crosslinked, SB(X)P(Q)-12/ $CHCl_3$ (B).

Sulfonation of S Block^{17,18}

To establish an adequate condition for sulfonation of S blocks, we tested several SB(X)S films of 50 μm thick, using 100% sulfuric acid (H_2SO_4),²¹ 5–10% (v/v) solution of chlorosulfonic acid (HSO_3Cl) in $CHCl_3$,¹⁹ both at room temperature, and concentrated H_2SO_4 containing silver sulfate (Ag_2SO_4) as a catalyst at 70°C.²² Test films were immersed in these agents for various periods of time, washed with distilled water, and dried at room temperature under vacuum of 10^{-3} torr for 2 days. The sulfonation in concentrated H_2SO_4 with Ag_2SO_4 at 70°C was so violent that the film was degraded into black charred fragments. On the other hand, the reaction in 100% H_2SO_4 at room temperature for 30 min was too mild; the sulfonic acid group was hardly detected by a conventional IR measurements.¹⁷ However, HSO_3Cl solution in $CHCl_3$ was found to be promising.

We chose 5% HSO_3Cl solution in $CHCl_3$ and followed the progress of sulfonation at room temperature by IR spectrometry. Quantitative determination of the degree of sulfonation by a conventional IR spectrometer was difficult because of the very low transmission of the sulfonated films. This difficulty could be circumvented by the high sensitivity, and data manipulation capabilities of the FT-IR spectrometer used here.

Poly(styrene-b-Butadiene-b-4-vinyl pyridine)

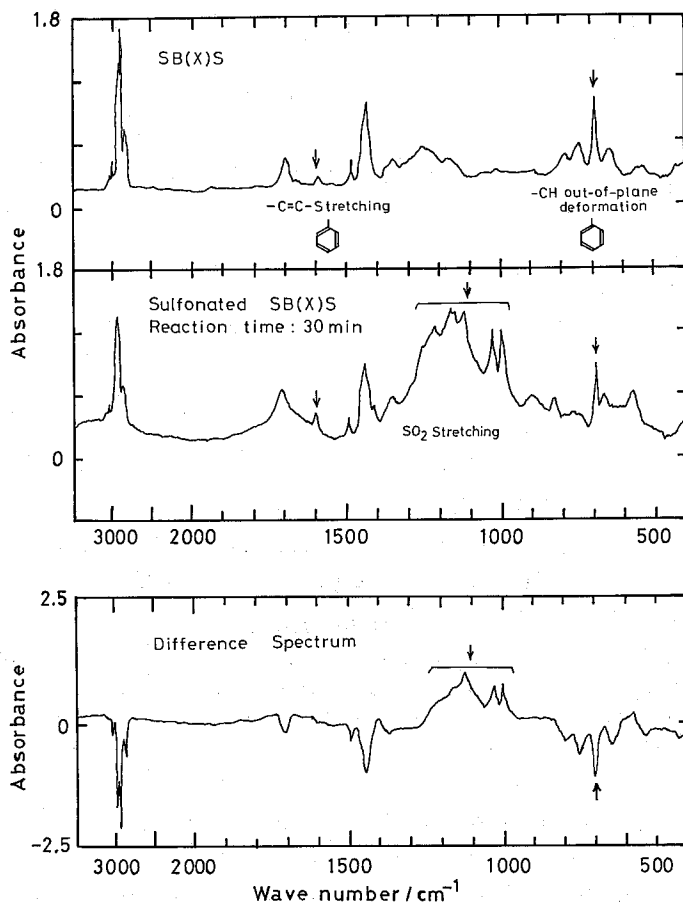


Figure 4. FT-IR transmission spectrum of an SB(X)S film sulfonated for 30 min in comparison with that of the original SB(X)S film, and difference spectrum between them.

Figure 4 shows FT-IR transmission spectra of an untreated SB(X)S film and that sulfonated for 30 min, and the difference spectrum. In the sulfonated film, the absorption band at 700 cm^{-1} corresponding to CH out-of-plane deformation mono-substituted benzene rings decreases, while the bands for SO_2 stretching vibration of sulfonic acid groups appear in 1010 to 1230 cm^{-1} range, as seen in the difference spectrum in Figure 4. The degree of sulfonation was estimated from the intensities of these bands. For the SO_2 stretching bands, the integrated intensity of all the bands was used. The C=C stretching vibration in benzene rings at 1600 cm^{-1} was used as the internal standard. Since sulfonation of polystyrene was known to occur preferentially in *para* position,²³ the integrated intensity of SO_2 bands in a poly(*p*-styrene sulfonic acid) sample was taken as the standard for complete sulfonation, i.e., the degree of sulfonation=1.

In Figure 5, the degree of sulfonation estimated from the 700 cm^{-1} and SO_2 bands for sulfonated SB(X)S films was plotted as a function of reaction time. The values obtained from the 700 cm^{-1} band show that all phenyl groups of S blocks have reacted with HSO_3Cl after 120 min reaction. However, the results from the SO_2 absorption

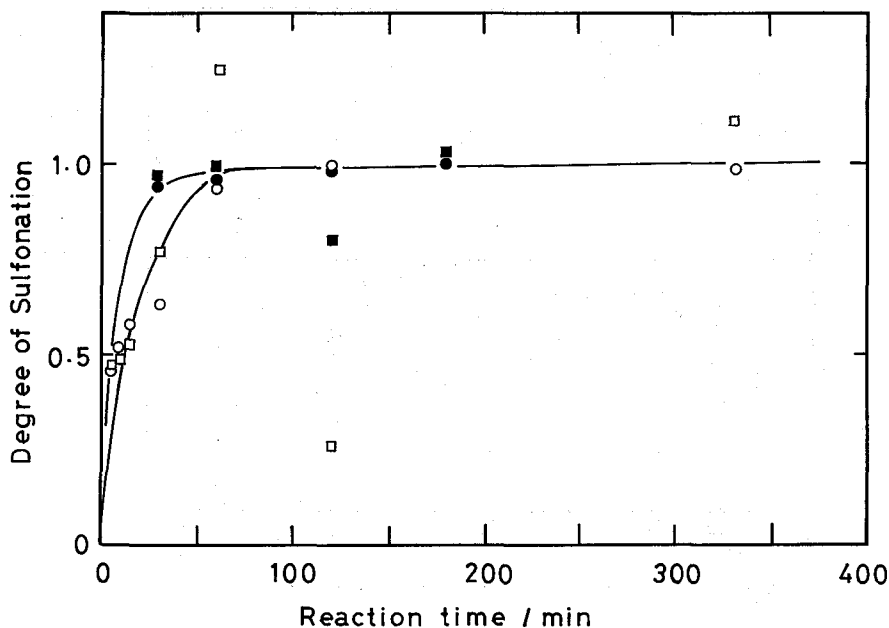


Figure 5. The degree of sulfonation as a function of reaction time for SB(X)S and SB(X)P(Q) films. The unfilled and filled symbols show the values for SB(X)S and SB(X)P(Q) films, respectively. Circles, estimated from 700 cm^{-1} bands; squares, estimated from SO_2 bands.

bands are consistent with those of the 700 cm^{-1} band only in the early stage of the reaction, but the two results deviate after 60 min. This suggests that some side reactions and disubstitution of the phenyl groups occur at the longer reaction time.

A possible side reaction is sulfone crosslinking ($-\text{SO}_2-$), particularly when HSO_3Cl is used as the sulfonating agent.^{24,25} Since the SO_2 absorption bands of sulfone appear at higher wave lengths than those of the sulfonic acid group, the integrated intensity of the SO_2 around $1000\text{--}1300\text{ cm}^{-1}$ decreases, leading to underestimation for the degree of reaction. By the di-substitution of phenyl groups, the degree of sulfonation estimated from the SO_2 bands should exceed one. Another possibility is that the remaining double bonds of B blocks might also participate the reaction with HSO_3Cl . These side reactions should be responsible for the difference between the results from 700 cm^{-1} and SO_2 bands.

We carried out sulfonation of SB(X)P(Q)-12/ CHCl_3 films of $50\text{ }\mu\text{m}$ thick with 5% HSO_3Cl solution to obtain S(S)B(X)P(Q)-12/ CHCl_3 films. The degree of sulfonation is also shown in Figure 5. The values estimated from the two different bands are consistent with each other within experimental error. Complete substitution of the phenyl groups again occur after about 120 min. The initial rate of reaction is larger in the SB(X)P(Q) films than that of the SB(X)S films, as compared from the data at the 30 min reaction. This seems to reflect the difference between the morphologies of the two films. The S domains in the SB(X)P(Q) films form a continuous phase, while those of the SB(X)S films disperse in a crosslinked B continuous phase. Therefore, the S

domains in the SB(X)S films swell in CHCl_3 at a slower rate than those in the SB(X)P(Q) films. This may explain the difference in the sulfonation rate.

Analysis of Chemically-Modified Surfaces

Coating of SBP-12 on the inner surface of a polyethylene tubing and the chemical modification of the coated film were carried out.⁹ At each step of the treatments, the surfaces were examined by ESCA.

In most cases, expected chemical elements were detected by ESCA. On the etched inner surface of polyethylene tubing, sulfur was detected. Probably, sulfonic acid groups were introduced into the surface during the etching process using chromic acid. In the C_{1s} spectrum of a SBP-coated tubing, the broad peak around the binding energy (BE) of 292 eV, attributable to the aromatic hydrocarbon, was observed in addition to the peak at 285 eV BE. On the SBP-coated surface, nitrogen of pyridine was also detected, but the sulfur found on the etched polyethylene surface was not detected. These results suggest that the polyethylene tubing was satisfactorily coated with the SBP polymer of the thickness, at least, more than the electron escape distance (50Å).

On the SBP(Q)-12 surface obtained after the quaternization, bromine was detected as expected, and the BE of N_{1s} core level shifted from 399.3 eV to 402.1 eV. On the SB(X)P(Q)-12 surface, bromine peak was hardly detectable, but two splitted peaks were observed in the Cl_{2p} spectrum, as shown in Figure 6. The peak at the higher BE is associated with covalently bonded Cl atoms introduced by the crosslinking reaction, while the peak at the lower BE corresponds to Cl^- ions. These findings indicate that the counter ion of the quaternary ammonium salt was converted from Br^- to Cl^- during the crosslinking reaction, at least, up to the 50Å depth from the surface.

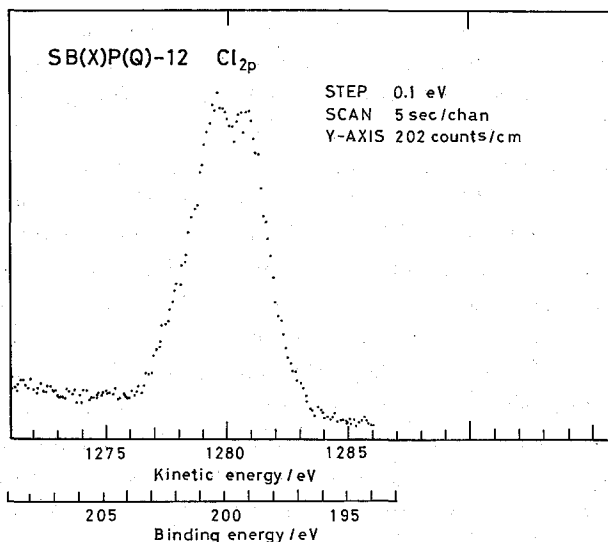


Figure 6. ESCA spectrum of Cl_{2p} core level for an SB(X)P(Q)-12 surface.

We tried to sulfonate the SB(X)P(Q) surface coated on the tubing with HSO_3Cl solution. However, the coated film was often peeled off during the treatment. Therefore, we examined sulfonation by HSO_3Cl vapor. First, we followed the process of the vapor-phase sulfonation of SB(X)S films as a control. SB(X)S films were exposed to HSO_3Cl vapor at 25°C under vacuum usually for 15 to 120 min. After the reaction, the films were washed with distilled water, and dried under vacuum. In these films, sulfonic acid groups were hardly detectable from FT-IR transmission spectra, while the SO_2 bands of sulfonic acid groups were found in their FT-IR ATR spectra as shown in Figure 7. The degree of sulfonation for the films at the 15 and 120 min reaction were

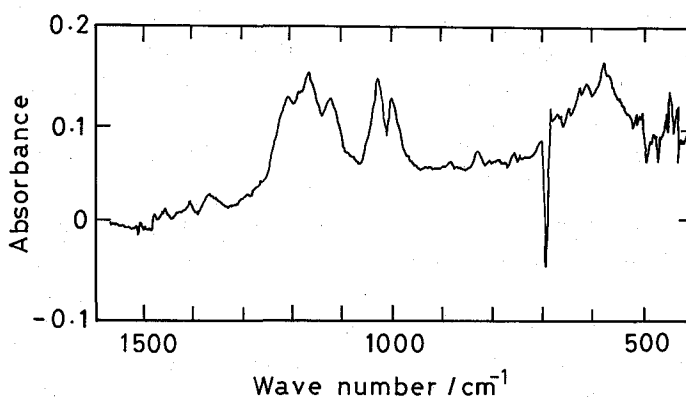


Figure 7. FT-IR ATR difference spectrum for the SB(X)S film sulfonated for 15 min by HSO_3Cl vapor.

estimated to be 0.57 and 0.87, respectively, under the penetration depth of about $1\ \mu\text{m}$ by the FT-IR ATR measurements. However, the cation-exchange capacities of this vapor-sulfonated films are usually as low as 0.002 m eq/g after 15 min reaction and 0.005 m eq/g even after 120 min reaction. These results demonstrate that the sulfonation took place first on the film surface and proceeded toward the inside with the prolonged reaction. Figure 8 shows ESCA spectra of S_{2p} core level for an SB(X)S film and those sulfonated for 15 and 120 min by HSO_3Cl vapor. In the untreated SB(X)S film (Figure 8(a)), only one peak corresponding to sulfur crosslinks is observed, while in the sulfonated films (Figure 8(b)-(f)) an additional peak is observed at the higher BE attributable to the sulfur of sulfonic acid groups. The relative height of the higher BE peak for the film sulfonated for 120 min (Figure 8(c)) is larger than that for 15 min (Figure 8(b)). Obviously, the degree of sulfonation on the surface increased with the reaction time. In order to examine the depth profile of sulfonation, we etched the film sulfonated for 120 min by Ar^+ ion sputtering. As shown in Figure 8(d)-(f), sulfonic acid groups decrease with increasing etching time. These results are consistent with those obtained from the FT-IR ATR experiments.

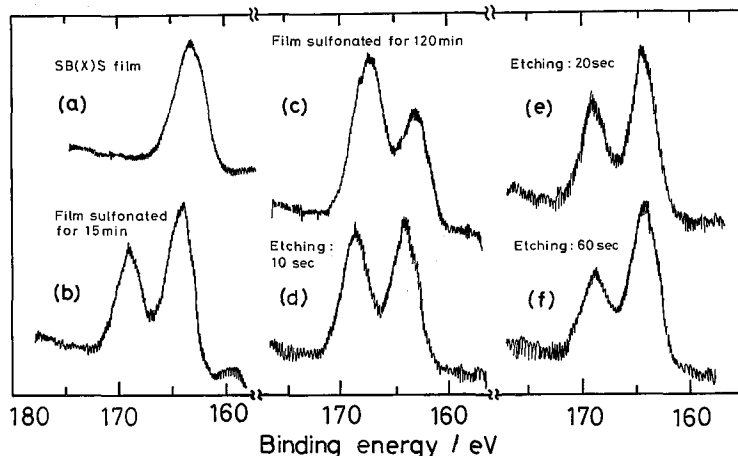


Figure 8. ESCA spectra of S_{2p} core level for an SB(X)S film and those sulfonated by HSO_3Cl vapor: (a) untreated SB(X)S film, (b) film sulfonated 15 min, and (c) film sulfonated for 120 min. The film sulfonated for 120 min was etched by Ar^+ ion sputtering for 10 sec (d), 20 sec (e), and 60 sec (f).

Ion-Exchange Capacities

Table III summarizes the results of ion-exchange capacities for sulfonated SB(X)S, SBP(Q)-12/ $CHCl_3$, SB(X)P(Q)-12/ $CHCl_3$, and S(S)B(X)P(Q)-12/ $CHCl_3$ films. The cation-exchange capacities, C^+ , for sulfonated SB(X)S films increase with the sulfonation time, while those for S(S)B(X)P(Q)-12 films exhibit a maximum at the sulfonation time of 60 min, and then decrease. To examine the relationship between the C^+ values and

Table III. Ion-Exchange Capacities (m eq/g) for Sulfonated SB(X)S and Ionized SBP Films

Sample Code	Sulfonation Time/min.	C^+	C^-	C^+/C^-	$C^+_{cal}^a$	$C^-_{cal}^a$	C^+/C^+_{cal}	C^-/C^-_{cal}
SB(X)S	5	0.36			0.54		0.67	
	10	0.57			0.63		0.90	
	15	0.72			0.68		1.06	
	30	0.76			0.74		1.13	
	60	1.42			1.06		1.34	
	120	1.32			1.33		1.17	
	330	1.94			1.10		1.76	
SBP(Q)-12	0		2.30			3.55		0.65
SB(X)P(Q)-12	0		1.53			2.45		0.63
S(S)B(X)P(Q)-12	30	0.91	1.77	0.52	1.17	2.22	0.78	0.80
	60	1.40	1.85	0.56	1.18	2.21	0.88	0.84
	120	1.19	2.02	0.59	1.21	2.21	0.98	0.91
	180	1.14	1.64	0.70	1.23	2.20	0.93	0.75

a. Calculated from the degree of sulfonation based on the 700 cm^{-1} band under the assumption of perfect quaternization and 75% crosslinking.

the degree of sulfonation, we calculated the ideal ion-exchange capacities, C^+_{cal} and C^-_{cal} , expected from the degree of sulfonation determined from 700 cm^{-1} band and the degree of quaternization. In this calculation, perfect quaternization of P blocks and 75% crosslinking of B blocks were assumed. Table III also shows such results.

The values of C^+/C^+_{cal} for the sulfonated SB(X)S films increase with the sulfonation time. The values larger than one found particularly for the films at 60 and 330 min reaction suggest that the di-substitution of phenyl groups and/or the sulfonation of the remaining double bonds of B blocks took place, as mentioned above. The small values of C^+/C^+_{cal} for the films sulfonated for 5–10 min show that only a part of the introduced sulfonic acid groups participates the ion-exchange. Presumably, this discrepancy is due to the low swellability of the slightly sulfonated films in the aqueous solution.

For sulfonated S(S)B(X)P(Q)-12 films, the values of C^+/C^+_{cal} increased with the sulfonation time till 120 min, a maximum value of 0.98 was attained, but appeared to decrease slightly at the longest sulfonation time of 180 min. For the anion-exchange capacities, the same trend was observed, although the maximum attainable value of C^-/C^-_{cal} was 0.91 for the 120 min sulfonation. The decrease in the C^+/C^+_{cal} and C^-/C^-_{cal} values for the films sulfonated for 180 min is presumably due to the fact that the sulfone crosslinks suppress the swellability of the sulfonated films.²⁵ A similar effect of crosslinking was also observed in the difference of C^-/C^-_{cal} between the SBP(Q)-12 and S(S)B(X)P(Q)-12 films.

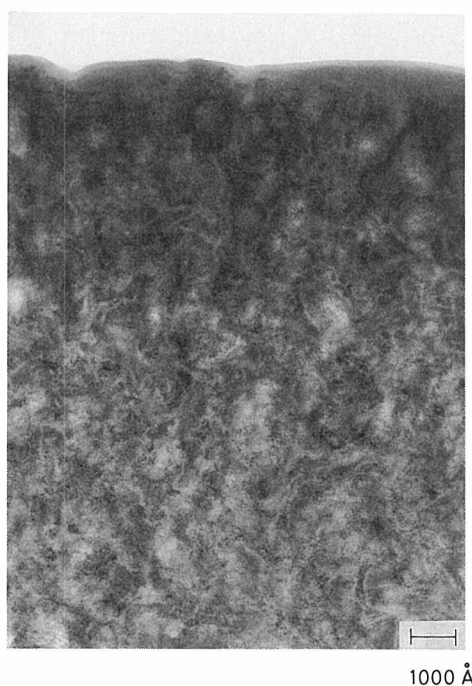


Figure 9. Electron micrograph of the SB(X)P(Q)-12 film sulfonated for 120 min.

Table III also shows the ratios between the cation- and anion-exchange capacities, C^+/C^- , for the S(S)B(X)P(Q)-12 films. Compared with the molar ratio (0.56) of styrene to pyridine unit in SBP-12, the C^+/C^- value for the film sulfonated for 180 min is very large. This suggests the existence of di-substituted phenyl groups and/or sulfonated B blocks in the film.

Morphology of S(S)B(X)P(Q) Film

Figure 9 shows an electron micrograph of an S(S)B(X)P(Q)-12/ CHCl_3 film treated for 120 min with 5% HSO_3Cl solution in CHCl_3 . The black regions are sulfonated S domains, the light regions, quaternized P domains, and the intermediate regions, crosslinked B domains. The "ball-in-a-box" morphology is significantly deformed, especially inside the film (compared with Figure 3). However, traces of the initial morphology are observed near the film surface. It is difficult to explain why the sulfonation destroyed the regular microphase structure maintained during the quaternization and crosslinking reactions. Formation of polyion complex between the opposite charged domains may not be the reason, since almost all of the introduced charge groups still possess the ion-exchange activity. Presumably, the sulfonation process of the S blocks may induce rearrangement of the microphase structure in the film to release the internal strain caused by the chemical modification as the S blocks form a continuous matrix in the "ball-in-a-box" morphology. The electrostatic interaction between the opposite charged domains might also be responsible for the destruction of the original film morphology. Regretfully, we can not give clear interpretation for this phenomenon at present.

Acknowledgements

This article is dedicated to Professor Emeritus Hiroshi Inagaki on the occasion of his retirement from Kyoto University. Two of the authors (H. O. and T. K.) sincerely thank him for his warm encouragement during their period in the Institute for Chemical Research, Kyoto University. The authors are greatly indebted to Professor Emeritus S. Ikeda and Prof. K. Kishi (present: Kwansei Gakuin University) of the Department of Chemistry, Osaka University, and to Dr. M. Matsumura and Mr. Y. Iwakabe of the the Laboratory for Chemical Conversion of Solar Energy, Osaka University for their kind help in ESCA experiments, and to Professor M. Kobayashi of this Department for kind guidance in FT-IR spectrum analysis. This research was supported in part by the Ministry of Education, Science and Culture (Monbusho) through the grant of Special Project Research (Professor T. Tsuruta, Science University of Tokyo, Coordinator), Design of Multiphase Biomedical Materials, Nos. 57219009 and 5811010, which were greatly acknowledged.

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